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ARTICLES

An Amperometric Sensor Based on Tin Dioxide and Cetylpyridinium Bromide Nanoparticles for the Determination of Vanillin

G. K. Ziyatdinova[a], *, T. S. Antonova[a], L. R. Mubarakova[a], and H. C. Budnikov[a]

[a] *Butlerov Institute of Chemistry, Kazan Federal University, Kazan, 420008 Russia*

**e-mail: Ziyatdinovag@mail.ru*

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Abstract—Voltammetric characteristics of vanillin are determined using electrodes modified with tin dioxide nanoparticles dispersed in surfactants of various nature in the Britton–Robinson buffer solution. The best characteristics are observed for a glassy carbon electrode modified by a dispersion of SnO_2 nanoparticles in cationic cetylpyridinium bromide (SnO_2–CPB/GCE). The electrode is characterized by cyclic voltammetry and electrochemical impedance spectroscopy. A fourfold increase in the effective surface area of SnO_2–CPB/GCE and a significant decrease in charge transfer resistance are shown in comparison with a GCE. The electrooxidation of vanillin proceeds irreversibly with the participation of two electrons and two protons and is controlled by the diffusion of the analyte. A sensor based on a SnO_2–CPB/GCE was developed to determine vanillin; it functions under conditions of differential pulse voltammetry. The analytical ranges for vanillin are 0.10–100 and 100–500 μM with the limits of detection and quantification 20 and 67 nM, respectively. The developed sensor is selective to vanillin in the presence of inorganic ions, saccharides, ascorbic acid, and a number of phenolic compounds. The sensor is used for the determination of vanillin in perfumes for household chemicals and vanilla essential oils. The results are in good agreement with the data of gas chromatography.

Keywords: voltammetry, chemically modified electrodes, nanoparticles of metal oxides, surfactants, vanillin

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Vanillin (4-hydroxy-3-methoxybenzaldehyde) has a wide range of practically useful properties. It is actively used in the food, pharmaceutical, and cosmetic industries as a flavor additive. Vanillin is a synthetic analog of natural vanilla, which up to this day is one of the most expensive flavors in the world market. Synthetic vanillin is obtained from guaiacol or lignin, which is a part of the wood and is a by-product of the pulp and paper industry [1]. Synthetic vanillin can cause headaches, nausea, and vomiting and also affect liver and kidney function [2]; therefore, affordable, selective, and sensitive methods for monitoring the concentration of vanillin are on demand.

Vanillin, like other phenolic compounds [3], rather easily enters the electron trnsfer reactions, which enables using electroanalysis methods for its determination. At present, chemically modified electrodes are actively used for the determination of vanillin, the main advantages of which are decreased redox potentials and increased selectivity and sensitivity of the determination because of masking of the so-called "chemical noises" [4]. Carbon nanomaterials (tubes, fibers, graphene), metal nanoparticles, polymer films, and their various combinations are most often used as electrode surface modifiers for the determination of vanillin (Table 1). Because of the modification of the electrode surface, it is possible to decrease the limits of detection for vanillin significantly (up to nanomoles) and expand the analytical range. Low limits of detection are achieved by the accumulation of vanillin or the product of its oxidation on the electrode surface under conditions of adsorptive and stripping voltammetry, respectively. In addition, the modified electrodes ensure the selectivity of the determination of vanillin in the presence of other electroactive compounds, for example, caffeine [14, 22]. Further improvement of chemically modified electrodes for the determination of vanillin, combining affordable and straightforward methods for their production with high analytical characteristics, is of theoretical and practical interest.

The goal of this work is to develop a new sensitive and selective amperometric sensor for vanillin based on SnO_2 nanoparticles and surfactants.

EXPERIMENTAL

Reagents and solutions. We used vanillin (99%) (Sigma-Aldrich, France); quercetin, morin hydrate (95%), and caffeic acid (98%) (Sigma, Germany), eugenol (99%) (Aldrich, Germany); and rutin trihydrate (97%) (Alfa Aesar, United Kingdom). Stock 0.01 M (0.001 M for rutin) solutions of the reagents were prepared by dissolving their accurately weighed